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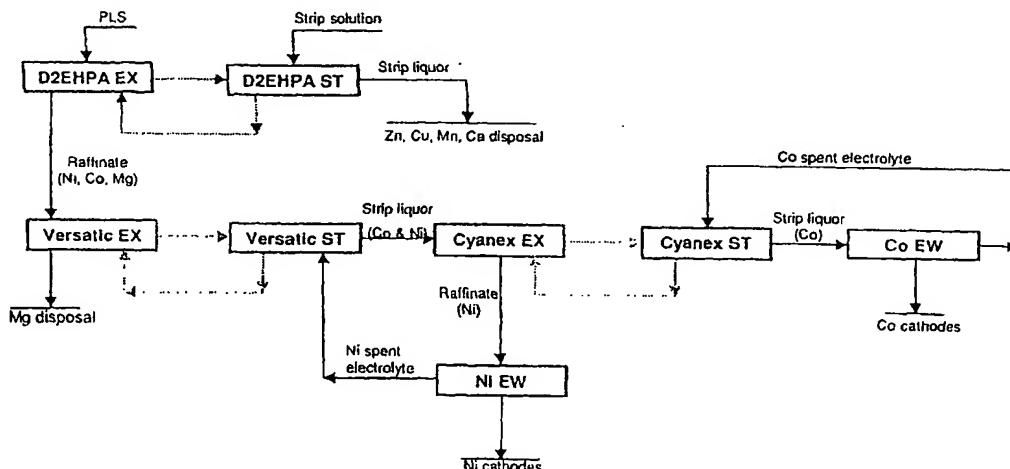
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**(54) Title: SOLVENT EXTRACTION PROCESS FOR RECOVERING NICKEL AND COBALT FROM LEACH SOLUTIONS**



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**(57) Abstract:** A method of separating nickel, cobalt or both from other cations contained in a leach solution, the method including the steps of subjecting the leach solution to separate solvent extraction steps using an organophosphoric acid, a carboxylic acid and an organophosphinic acid.

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SOLVENT EXTRACTION PROCESS FOR RECOVERING NICKEL AND COBALT  
FROM LEACH SOLUTIONS

5 The present invention relates to a method of  
separating cobalt and nickel from other elements contained  
in an aqueous leach solution.

10 The world mineral industry is experiencing an  
unprecedented interest in nickel-cobalt extraction from  
laterite ores through high pressure acid leach (HPAL) and  
solvent extraction - electrowinning (SX-EW) processes. In  
WA, three nickel laterite projects have been commissioned.  
These are the Cawse project of Centaur Mining Ltd, the  
15 Bulong project of Preston Resources and the Murrin Murrin  
project of Anaconda Nickel Ltd. The HPAL process for the  
three projects is very similar, however the down stream  
processes (including SX) differ substantially.

20 In the Murrin Murrin process (Motteram et al.,  
1996), a sulfide precipitation is used to separate the  
nickel, cobalt, copper and zinc from impurities such as  
calcium, magnesium and manganese which remain in the leach  
solution. After solids/liquid separation, the nickel,  
cobalt, copper and zinc are re-leached under pressure with  
25 acid. Further solution purification is needed to separate  
nickel and cobalt from copper and zinc. The cobalt is then  
separated from nickel by solvent extraction with Cyanex  
272. The nickel and cobalt are recovered by reduction with  
hydrogen. The drawbacks of the Murrin Murrin process are:  
30 • The separation of manganese from cobalt by sulphide  
precipitation is incomplete and causes problems in the  
downstream processes,  
• The leaching of sulphides needs high pressure and high  
temperature, indicating high capital and operating  
35 costs.  
• The separation of other impurities such as copper and  
zinc from nickel and cobalt needs separate processes.

In the Cawse process (Manson et al., 1997), a hydroxide precipitation is used to separate the impurities such as calcium, magnesium and manganese (partly). After 5 solids/liquid separation, the nickel, cobalt, copper and zinc are re-leached with an ammoniacal solution. Nickel and copper are separated from cobalt and zinc by solvent extraction with LIX84I. Further solution purification is needed to separate nickel from copper and cobalt from zinc. 10 The nickel is recovered by electrowinning while cobalt is precipitated as sulphide. The drawbacks of the Cawse process are:

- The use of ammoniacal leaching to separate manganese from cobalt results in complexity of the flowsheet and 15 causes serious problems in the downstream processes,
- The reductive stripping of cobalt from organic extractant and the re-oxidation of the organic extractant cause organic degradation (Kindred, 2000), which in turn results in crud formation,
- Ammonia is expensive and the scrubbing and recovery of ammonia are difficult,
- Cobalt product containing zinc is a semi-product, indicating revenue loss.

25 The Bulong process (Taylor and Cairns, 1997), uses a direct solvent extraction approach. Cobalt, copper, zinc and manganese are separated from nickel, calcium and magnesium by solvent extraction with Cyanex 272. The nickel in the raffinate is separated from calcium and magnesium by 30 solvent extraction with Versatic 10 and then electrowon. The solution containing cobalt, copper, zinc and manganese is subjected to sulphide precipitation, solids/liquid separation and acid pressure re-leach to separate cobalt, copper and zinc from manganese. The copper is eliminated 35 from the solution by ion exchange and zinc by solvent extraction with D2EHPA. The cobalt is then recovered from the purified solution by electrowinning. The drawbacks of

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the Bulong process are:

- Manganese is separated from cobalt by sulphide precipitation and other impurities are separated by different further processes (ion exchange and further SX),
- Gypsum precipitation occurs in both Cyanex 272 and Versatic 10 circuits,
- Aqueous feed solution with its original volume is treated twice - in both the Cyanex and Versatic 10 SX circuits. This requires larger circuits (higher capital expenditure) than if the valuable metal (nickel) were concentrated by extraction into the organic phase in the first circuit.

15           Currently used processes all incorporate precipitation and re-leach steps. Bulong and Murrin Murrin employ sulfide precipitation and acid re-leach, whereas Cawse employs hydroxide precipitation and ammoniacal re-leach. These steps require additional chemical reagents, 20 precipitation, separation and leaching equipment, and additional operating costs.

25           Recovery of nickel and cobalt from purified leach solutions by electrowinning, precipitation or any other appropriate process, is best performed after the metals have been concentrated to an appropriate level (often of the order of 50g/L). In laterite leach solutions, typical nickel and cobalt concentrations may be 1.0 - 4.0 g/L nickel and 0.1 - 0.4 g/L cobalt.

30           An object of the present invention is to provide processes for separating cobalt and nickel from impurities contained in leach solutions that concentrate the nickel and cobalt to levels appropriate for recovery by 35 electrowinning, precipitation or any other appropriate process.

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According to the present invention there are provided methods of separating nickel, cobalt or both from other cations contained in a leach solution, the method including the steps of subjecting the leach solution to 5 separate solvent extraction steps using an organophosphoric acid, a carboxylic acid and an organophosphinic acid.

In a preferred embodiment of the invention, the carboxylic acid extraction step is conducted with a mixture 10 of carboxylic acid and a synergist that is capable of increasing the pH gap,  $\Delta pH_{50}$ , between isotherms for nickel and cobalt and those for manganese and calcium. However, the use of the synergist is not always required. Whether or not a synergist is used will depend on the ordering of 15 the three solvent extraction steps, and the cations present on the liquor being subjected to the octacarboxylic acid solvent extraction.

The  $pH_{50}$  value is the pH at which 50% metal 20 extraction is achieved. Thus,  $\Delta pH_{50}$  is the difference between the  $pH_{50}$  values for two metals.

In another embodiment of the present invention, there is provided a method for separating nickel, cobalt or 25 both from other cations contained in a leach solution, the method involving subjecting the leach solution to separate solvent extraction steps using:  
(a) an organophosphinic acid; and  
(b) a carboxylic acid in combination with a synergist that 30 is capable of increasing the pH gap,  $\Delta pH_{50}$ , between isotherms for nickel and cobalt and those for manganese and calcium.

In the most preferred embodiment of the 35 invention, the carboxylic acid is 2-hexyl, 2-methyl octacarboxylic acid or a carboxylic acid having extraction characteristics similar to or the same as 2-hexyl, 2-methyl

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octacarboxylic acid. The term carboxylic acid is used in its broadest sense to refer to any organic carboxylic acid. Carboxylic acids have the formula RCOOH, in which R represents any optionally substituted aliphatic or aromatic 5 group, or combinations of these groups, including optionally substituted alkyl, alkenyl, alkynyl, aryl, or heteroaryl groups (and combinations thereof). Preferably R represents a relatively bulky group containing at least 4 carbon atoms, and preferably between 4 to 18 carbon atoms.

10

The organophosphoric acid is most preferably di-2-ethylhexyl phosphoric acid (D2EHPA), however it will be appreciated by persons skilled in the art that an organophosphoric acid having extraction characteristics 15 similar to D2EHPA could be used. Organophosphoric acids have the formula  $(RO)_2PO_2H$ , in which R represents an organic group. The two organic groups R, which may be the same or different, can be selected from optionally substituted branched, straight chained or cyclic alkyl, 20 alkenyl or alkynyl groups. Preferably the organic groups are fairly bulky, and have a minimum of 4 carbon atoms, more preferably from 6 to 18 carbon atoms. The organic groups may suitably be n-octyl, cyclooctyl or 2-ethylhexyl.

25

In the most preferred embodiment of the invention, the organophosphinic acid is di-2,4,4-trimethylpentyl phosphinic acid (eg Cyanex 272). However it will be appreciated by persons skilled in the art that any organophosphinic acid having extraction 30 characteristics similar to di-2,4,4-trimethylpentyl phosphinic acid could be used. Organophosphinic acids have the formula  $R_2PO_2H$ , in which R represents an organic group. The two organic groups R, which may be the same or different, can be selected from optionally substituted 35 branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups. Preferably the organic groups are fairly bulky, and have a minimum of 4 carbon atoms, more

preferably from 6 to 18 carbon atoms. The organic groups are preferably unsubstituted branched, straight chained or cyclic alkyl groups, and may suitably be n-octyl, cyclooctyl, 2-ethylhexyl or 2,4,4-trimethylpentyl.

5

The term "alkyl" used either alone or in a compound word such as "optionally substituted alkyl" or "optionally substituted cycloalkyl" denotes straight chain, branched or mono- or poly- cyclic alkyl, preferably C1-30

10 alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isbutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3- or 4-butylloctyl, 1-2-pentylheptyl and the like. Examples of cyclic alkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl and the like. The alkyl may 35 optionally be substituted by any non-deleterious substituent.

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In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, 5 haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, 10 dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, halo(heterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, 15 alkylthio, benzylthio, acylthio and the like.

Suitable optional substituents will be chosen on the basis that the organophosphinic or organophosphoric acid have the desired extraction characteristics, and the 20 substituents do not react with any other component of the mixture under the given extraction conditions.

The term "halogen" denotes fluorine, chlorine, bromine or iodine.

25 A range of different compounds may be used as the synergist, such as pyridine carboxylate esters, phosphine oxides or oximes (particularly non-chelating oximes). However the synergist is preferably a pyridine carboxylate 30 ester.

The term "pyridine carboxylate ester" is used this specification in its broadest sense to refer to any organic compound containing at least one pyridine group and 35 at least one carboxylate group. Accordingly, the term encompasses 2-pyridine carboxylates, 3-pyridine carboxylates, 4-pyridine carboxylates, and dicarboxylates

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of pyridine such as 3,5-pyridine dicarboxylates. The ester groups may be based on optionally substituted aliphatic hydrocarbon groups including branched, straight chained or cyclic alkyl, alkenyl and alkynyl groups. Preferably the 5 aliphatic hydrocarbon groups have between 4 and 18 carbon atoms, and therefore include n-octyl, 2-ethylhexyl and cyclooctyl groups.

The term "oxime" is used in this specification in 10 its broadest sense to refer to any organic compound containing a carbon to nitrogen double bond, with the nitrogen atom being attached to an oxygen atom. Accordingly, the term oxime includes within its scope 15 oximes with a hydroxy group attached to the nitrogen atom, and oxime ethers.

The organic phase for the organophosphoric acid' extraction step includes a modifier in addition to an organophosphoric acid. The organic phase for the 20 organophosphinic acid extraction step similarly includes a modifier in addition to an organophosphoric acid.

The modifier is any suitable modifier that improves separation of the organic and aqueous phases. 25 Suitable modifiers include 2-ethylhexanol, isodecanol and isotridecanol and tri n-butyl phosphate (TBP). TBP is the preferred modifier.

The organic solvent may be any suitable organic 30 solvent for the organophosphoric acid that achieves good phase separation from the aqueous phase with the modifier. In some respects the organic solvent could be considered to be a diluent for the extraction agent. Kerosene is the most common solvent/diluent used for this purpose due to 35 its low cost and availability.

The loaded organic phase resulting from solvent

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extraction with organophosphoric acid may be scrubbed with an aqueous scrub solution containing manganese and copper. This aqueous scrub solution is preferably obtained by conducting a selective strip on a scrubbed loaded organic 5 solution produced in the scrubbing step, and recycling the manganese and copper containing aqueous solution back to the scrubbing stage to be used as the aqueous scrub solution. A spent aqueous scrub solution generated in the scrubbing step is then recycled to the leach solution to 10 maximise the recovery of cobalt (and nickel if present at that stage of the process). The selectively stripped organic solution would usually then be subjected to bulk stripping to remove a large proportion of the cations remaining therein to be recycled for use as the organic 15 phase in the initial extraction step.

The scrubbed organic solution may be selectively stripped of manganese and copper by contacting it with an acid. Sulphuric acid is preferred due to its low cost, 20 however other acids such as HCl and HNO<sub>3</sub> could be used. The bulk stripping can be conducted by contacting the selectively stripped organic solution with a second acid. The second acid needs to be stronger than the first. Accordingly, when sulphuric acid is used as the first acid, 25 more concentrated sulphuric acid or hydrochloric acid may be used as the second acid to bulk strip the selectively stripped organic solution of the impurity elements. The bulk stripped organic solution may then be recycled for use as the organic phase in the initial extraction step.

30

The range of the Mn and Cu in the aqueous scrub solution will depend on how much Co (and Ni) is to be scrubbed and the aqueous to organic (A/O) ratio. Preferably, the mole ratio of (Mn+Cu)/(Co+Ni) is at least 35 1.5 for complete scrubbing.

The amount of organophosphoric acid in the

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organic solution used in the organophosphoric acid extraction step will depend on the concentration of the elements to be extracted and the A/O ratio, however the amount would typically be in the range of from 3% to 35%

5 v/v, with a preferred range of 5% to 25%. At levels above 35% the organic solution will be too viscous resulting in lower extraction kinetics.

The amount of modifier in the organic solution 10 used in the organophosphoric acid extraction step will also vary. The range of modifier will typically be in the range of 3% to 15% v/v, with a preferred range of 5% to 10%.

Preferably, the pH of the aqueous phase is 15 maintained in a range from 3.0 to 4.5 and more preferably 3.5 to 4.0 in the organophosphoric acid extraction. The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst temperatures as low as 10°C are achievable, a temperature 20 lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic phase.

The aqueous to organic ratio (A/O) in the 25 extraction stage of the organophosphoric acid extraction step is most preferably 1:1, but may lie in the range from 10:1 to 1:10, and preferably 1:2 to 5:1. The aqueous to organic ratio maintained in the scrubbing stage of this step may lie within the range of from 1:5 to 1:200, but 30 preferably it is in the range of 1:5 to 1:20, and most suitably it is from 1:5 to 1:10.

The amount of organophosphinic acid in the 35 organic solution used in the organophosphinic acid solvent extraction step will depend on the concentration of the elements to be extracted and the A/O ratio, however the amount would typically be in the range of from 3% to 35%

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v/v, with a preferred range of 5% to 25%. At levels above 35% the organic solution will be too viscous resulting in lower extraction kinetics.

5           Preferably, the pH of the aqueous phase is maintained in a range from 5.0 to 6.0 in the organophosphinic acid solvent extraction circuit. The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst 10 temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic phase.

15           The aqueous to organic ratio (A/O) in the organophosphinic acid solvent extraction circuit is most preferably 1:1, but may lie in the range from 3:1 to 1:3.

20           The cobalt extracted into the loaded organic phase in the organophosphinic acid extraction circuit is stripped therefrom in a stripping stage. In the stripping stage, the A/O ratio may be from 1:2 up to 1:200, and the pH from 2.0 to 4.0. Other details concerning the organophosphinic acid extraction stage are well within the 25 knowledge and experience of persons in the art of the invention.

30           The steps outlined above can be conducted in combination with other solvent extraction steps and optionally one or more precipitation steps to separate certain elements from each other. For instance, it is common in the art of the invention for a preliminary iron precipitation step to be conducted to precipitate out iron to leave an aqueous leach solution containing the target 35 elements. However, it is a major advantage of the process of the present invention that precipitation steps involving precipitation out of the target elements (such as cobalt

and nickel) and re-leaching of the precipitate can be avoided. Even when such a precipitation step is required, it is to be noted that no precipitation steps for the purpose of separating manganese from cobalt are required.

5 Therefore, in a preferred embodiment of the invention the process does not include a sulphide precipitation stage for separating cobalt from manganese. In a more preferred embodiment of the invention, the process does not include a precipitation step involving precipitation out of the

10 target elements and re-leaching of the precipitate.

It will be well understood to persons skilled in the art of the invention that scrubbing stages of the type well known in the art may be used for recovering elements

15 even if the scrubbing stages are not specifically mentioned. The design of the optimum arrangement of scrubbing stages will depend on the specific aqueous leach solution and the elements desired to be recovered therefrom (and target percentage recovery levels).

20

According to the present invention there is also provided a plant for conducting the method described above, the plant including, in any order:

- a carboxylic acid solvent extraction circuit including a carboxylic acid solvent extractor and a carboxylic acid stripper;
- an organophosphoric acid solvent extraction circuit including an organophosphoric acid solvent extractor and an organophosphoric acid stripper; and
- 30 - an organophosphinic acid solvent extraction circuit including an organophosphinic acid solvent extractor and an organophosphinic acid stripper.

35 Preferably the organophosphoric acid extraction circuit includes:

- a scrubber for scrubbing the loaded organic solution generated in solvent extractor;

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- a selective stripper in which the scrubbed organic solution generated in the scrubber is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubber;
- 5 - a scrubbed organic solution conduit for conducting the scrubbed organic solution to the selective stripper;
- an aqueous scrub solution conduit for conducting the aqueous scrub solution from the selective stripper to the scrubber; and
- 10 - a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubber to the organophosphoric acid solvent extractor.

Preferably the plant further includes an organic solution recycle conduit for conducting the partially stripped scrubbed solution from the stripper to the organophosphoric acid solvent extractor. More preferably, a bulk stripper is located in this recycle conduit, in which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extractor.

As will be understood to persons skilled in the art of the invention, the various solvent extractors are preferably countercurrent solvent extractors. In addition, further scrubbing stages and vessels or tanks may be included in the plant.

The plants described above will also include the necessary conduits for passing the subject streams from one vessel, stage or circuit to the next. The plants will also usually include a cobalt recovery stage and a nickel recovery stage. The cobalt recovery stage may include a cobalt precipitation vessel or an electrolytic cell in which a cobalt electrowinning process can be conducted. The nickel recovery stage may include a nickel electrolytic cell in which a nickel electrowinning process can be

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conducted. The arrangement of an appropriate plant including all of these elements is well within the skill of a person in the art of the invention now that the direction has been provided to conduct the process for recovering 5 cobalt in the manner described above.

Some preferred embodiments of the invention are described in the accompanying examples and figures, in which:

10 Figure 1 illustrates a flow chart for the one stage in the processes of the preferred embodiments of the invention as represented in Figures 2 and 4-5, and represents schematically a part of the plants of those preferred embodiments of the invention;

15 Figure 2 illustrates a schematic flow chart for one embodiment of the process of the invention, and represents schematically a plant for this embodiment of the invention;

20 Figure 3 illustrates a schematic flow chart for a second embodiment of the process of the invention (in which the organophosphoric acid extraction circuit is not used), and represents schematically a plant for this embodiment of the invention;

25 Figures 4 and 5 illustrate a schematic flow chart for third and fourth embodiments of the process of the invention, and represent schematically plants for these embodiments of the invention.

In the embodiments of the preferred embodiments 30 of the invention, Versatic (2-hexyl 2-methyl octacarboxylic acid) is used as the octacarboxylic acid (in kerosene organic solvent), Cyanex 272 (di-2,4,4-trimethylpentyl phosphinic acid) is used as the organophosphinic acid, and D2EHPA (di-2-ethylhexyl phosphoric acid) is used as the 35 organophosphoric acid.

Flow sheets for four alternative embodiments of

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the invention are illustrated in Figures 2 to 5. In the embodiments represented in Figures 2 and 4 to 5, the boxes referring to "D2EHPA SX" (di-2-ethylhexyl phosphoric acid solvent extraction) in combination with the boxes "D2EHPA 5 ST" (ST = strip) should be understood to be a short-hand reference to all of the steps outlined in Figure 1.

The organophosphoric acid extraction stage, which is a feature of the processes of the first, third and 10 fourth preferred embodiments of the invention, is described in detail in Figure 1. An aqueous leach solution 1 (which may be the PLS - plant leach solution - in Figure 2, the strip liquor from the Versatic strip in Figure 4, or the strip liquor from the Cyanex strip in Figure 5) is fed into 15 a countercurrent solvent extractor 2 in which the aqueous leach solution 1 is contacted with an organic extractant solution 3 comprising a solution of an organophosphoric acid (D2EHPA) and a modifier (TBP) in an organic solvent (kerosene). The aqueous raffinate 4 from the solvent 20 extraction contains most of the cobalt (and nickel, if present in the aqueous leach solution 1) and, to the extent that it is present, a large proportion of the magnesium, from which the cobalt (and nickel) may be recovered.

25 The loaded organic liquor 5 from the solvent extractor 2 is scrubbed in a scrubber 6 with a scrub solution 7 containing manganese and copper. Scrubbed loaded organic solution 8 is selectively stripped with a first acid, a dilute sulphuric acid 9, in a stripper 10 to 30 form scrub solution 7, part of which is recycled to scrubber 6. Partially stripped organic extractant 11 is then stripped of all impurities with a second acid, dilute hydrochloric acid 12, in a bulk stripper 13. Stripped organic solution 3 is recycled to extractor 2.

35

Figure 2 is a flow chart illustrating a process which combines an initial solvent extraction process using

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di-2-ethylhexyl phosphoric acid (D2EHPA) with two further solvent extraction processes using 2-hexyl, 2-methyl octacarboxylic acid (Versatic 10) and an organophosphinic acid respectively, to recover nickel and cobalt.

5

Figure 3 is a flow chart illustrating a process which combines a synergistic SX process using 2-hexyl, 2-methyl octacarboxylic acid (Versatic 10) as extractant and a synergist, with a further SX process using an 10 organophosphinic acid, to recover nickel and cobalt.

Figures 4 and 5 illustrate a process which combines a synergistic SX process using 2-hexyl, 2-methyl octacarboxylic acid (Versatic 10) as extractant and a synergist, with two further SX processes using di-2-15 ethylhexyl phosphoric acid (D2EHPA) and an organophosphinic acid respectively, to recover nickel and cobalt. This process is more robust than the process described with reference to Figure 3.

20

Figure 4 shows a flow chart in which 2-hexyl, 2-methyl octacarboxylic acid (Versatic 10) and a synergist such as pyridine carboxylate ester (Acorga CLX50 - a commercially available pyridine carboxylate diester) are 25 used in the first solvent extraction stage, di-2-ethylhexyl phosphoric acid (D2EHPA) is used in the second solvent extraction stage and the organophosphinic acid di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) is used in the third solvent extraction stage. Figure 5 shows the 30 situation when the latter two SX stages are reversed such that 2-hexyl, 2-methyl octacarboxylic acid (Versatic 10) and a synergist such as pyridine carboxylate ester (Acorga CLX50) are used in the first solvent extraction stage, the organophosphinic acid di-2,4,4-trimethylpentyl 35 phosphinic acid (Cyanex 272) is used in the second solvent extraction stage and di-2-ethylhexyl phosphoric acid (D2EHPA) is used in the third solvent extraction stage.

More specifically, as shown in Figure 1,

5 (a) Zinc, calcium, copper and manganese are separated from nickel, cobalt and magnesium using D2EHPA. The loaded organic phase resulting from solvent extraction with D2EHPA may be scrubbed with an aqueous solution containing manganese and copper. The aqueous scrub solution may then be recycled to the leach solution to maximise the recovery of cobalt and nickel (Fig 1).

10 (b) Versatic 10 is used to separate nickel and cobalt from magnesium. Nickel and cobalt are concentrated by stripping at a high organic/aqueous (O/A) flowrate ratio (Fig. 2)

15 (c) An organophosphinic acid is used to separate cobalt from nickel. Cobalt is further concentrated by stripping at a high O/A flow rate ratio,

20 (d) Both nickel and cobalt could be recovered by electrowinning, precipitation or any other appropriate method.

20 In a less-favoured variation of this process, the order of the Versatic 10 and organophosphic acid SX processes could be reversed, however this would result in the cobalt only being concentrated through one extraction/stripping cycle making its recovery (by electrowinning or precipitation or any other appropriate process) less favourable.

More specifically in Figure 3,

30 (a) Nickel, cobalt, zinc and copper are separated from calcium, magnesium and manganese by synergistic solvent extraction using Versatic 10 and a synergist. Scrubbing will be required for complete separation of the cobalt and manganese.

35 (b) Nickel, cobalt and zinc are concentrated by stripping the loaded organic solution with a high O/A flowrate ratio in the first stripping stage,

- 18 -

- (c) Copper is then stripped in a second stage with stronger acid and separated as a by-product,
- (d) Zinc and cobalt are separated from nickel by solvent extraction using an organophosphinic acid,
- 5 (e) Cobalt is concentrated by stripping the loaded organic solution with a high O/A flowrate ratio in the first stripping stage,
- (f) Zinc is then stripped in a second stage with stronger acid and separated as a by-product,
- 10 (g) Nickel and cobalt can be recovered by either electrowinning, precipitation or any other appropriate process

More specifically in Figure 4,

- 15 (a) Nickel, cobalt, zinc and copper are separated from calcium, magnesium and manganese by synergistic solvent extraction using Versatic 10 and a synergist. Scrubbing may not be required for complete separation of the cobalt and manganese as manganese can be
- 20 separated in the next SX process step. The synergist is necessary to effect complete separation of the Ca (to the raffinate) during extraction and thereby prevent gypsum precipitation during stripping. If the leach solution entering solvent extraction has only a
- 25 low calcium concentration, use of the synergist may not be necessary as calcium can also be separated in the next SX process step.
- (b) Nickel, cobalt and zinc (and any remaining manganese) are concentrated by stripping the loaded organic
- 30 solution with a high O/A flowrate ratio in the first stripping stage,
- (c) Copper is then stripped with stronger acid and separated as a by-product (alternatively, a bulk strip can be used, in which case copper will also be
- 35 concentrated with the nickel cobalt and zinc),
- (d) Zinc (and any remaining copper, manganese and calcium) are separated from the nickel and cobalt using D2EHPA,

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- (e) Cobalt is separated from nickel by solvent extraction using an organophosphoric acid,
- (f) Cobalt is concentrated by stripping the loaded organic solution with a high O/A flowrate ratio,
- 5 (g) Nickel and cobalt can be recovered by either electrowinning, precipitation or any other appropriate process.

10 In a variation of this process, the order of the D2EHPA and organophosphoric acid SX processes could be reversed (Fig 5). Figure 5 shows cobalt being recovered by precipitation. Alternatively, cobalt could be electrowon with the spent electrolyte being returned to the organophosphoric acid strip circuit.

15

A synergist is used with Versatic 10 in processes 2 and 3 to help separate manganese and calcium from nickel and cobalt. The synergistic effect is to move the nickel and cobalt isotherms to lower pH values, thereby increasing 20 the pH gap ( $\Delta\text{pH}_{50}$ ) to the manganese and calcium isotherms and thus promoting better separation. Pyridine-based synergists such as pyridine carboxylate ester (Acorga CLX50) have proved suitable for this purpose. Other synergists demonstrating a similar effect may be used.

25

The preferred embodiments described above will now be described in further detail with reference to the accompanying examples.

30 EXAMPLE 1 (Fig 4)

Synergistic solvent extraction with Versatic 10 and CLX50.

The aim of synergistic solvent extraction with Versatic 10 and CLX50 is to promote separation of nickel and cobalt from manganese and calcium by increasing the pH 35 gap,  $\Delta\text{pH}_{50}$ , between their respective isotherms. Copper and zinc extract with the nickel and cobalt; magnesium reports to the raffinate with the manganese and calcium

pH isotherms and distribution isotherms were determined with Versatic 10 and CLX50. The pH isotherms of nickel and cobalt with Versatic 10 were significantly affected by the addition of CLX50. As a result, the addition of CLX50 as a synergist substantially enlarged the  $\Delta\text{pH}_{50}$  difference between cobalt and manganese pH isotherms. The  $\Delta\text{pH}_{50}$  between manganese and cobalt increased from 0.28 pH units without CLX50 to 0.85 pH units with 20% CLX50 as synergist. The  $\Delta\text{pH}_{50}$  between calcium and nickel increased from 0.77 pH units without CLX50 to 1.87 pH units with 20% CLX50 as synergist. Shellsol 2046 was used as diluent in these experiments.

15 EXAMPLE 2 (Figs 1, 4 and 5)

Separation of nickel and cobalt from manganese and other impurities, using a synthetic nickel laterite acid leach solution.

20 1. Extraction with D2EHPA

The aim of the extraction with D2EHPA is to extract all the zinc, calcium, copper and manganese from the aqueous leach solution (PLS) into the organic D2EHPA solution and to minimise the extraction of cobalt, nickel and magnesium.

25 The aqueous solution was a synthetic iron-free laterite leach solution containing 2.60 g/L Ni, 0.24 g/L Co, 0.27 g/L Zn, 0.52 g/L Ca, 0.09 g/L Cu, 1.87 g/L Mn and 2.89 g/L Mg. The organic solution consisted of 12% di-2-ethylhexyl phosphoric acid (D2EHPA), 2.5% tri-n-butyl phosphate (TBP) and 85.5% kerosene (Shellsol 2046), all by volume. Four counter-current extraction stages were used at an A/O flowrate ratio of 1:1. The pH in the four mixers was controlled at 3.7 using three pH controllers with the addition of ammonia solution (Fig 1). The results are shown in Table 1. All the zinc, calcium, manganese and copper

were extracted in four stages. Some 12.6% of the cobalt, 20% of the magnesium and no nickel were co-extracted. The raffinate contained only cobalt, nickel and magnesium.

5           If the D2EHPA extraction described above had been preceded by synergistic SX with Versatic 10 and CLX50, Mg and Ca would already have been removed (Figs 3 and 4), leaving only Co and Ni in the D2EHPA raffinate (Fig 4). The Ni/Co raffinate could then proceed to a subsequent 10 solvent extraction step where cobalt would be extracted from the aqueous solution by di-2, 4, 4-trimethylpentyl phosphinic acid (Cyanex 272), using a well proven commercial process. The cobalt and nickel could be then recovered by electrowinning from the Cyanex strip and 15 raffinate solutions respectively (Fig 4).

Alternatively, if the D2EHPA extraction described above had been preceded by both synergistic SX with Versatic 10 and CLX50 and a known Cyanex 272 extraction, 20 Ni, Mg and Ca would already have been removed, leaving only Co in the D2EHPA raffinate, which could be recovered by hydroxide precipitation (Fig 5), or by electrowinning with the cobalt electrowinning spent electrolyte containing sulphuric acid being recycled to the Cyanex strip. Ni 25 could be recovered by electrowinning from the Cyanex raffinate.

In both flowsheet configurations (Figs 4 and 5), the nickel electrowinning spent electrolyte containing 30 sulfuric acid would be recycled to the Versatic 10 strip.

Table 1 Summary of semi-continuous extraction test results

Metal name	Concentration (g/L)			Total extraction (%)
	In feed	In loaded organic	In raffinate	
Zn	0.265	0.255	0.000	100.00
Ca	0.516	0.605	0.000	100.00
Mn	1.865	1.775	0.000	100.00
Cu	0.094	0.089	0.000	100.00
Co	0.240	0.031	0.196	12.57
Ni	2.597	0.000	2.535	0.000
Mg	2.893	0.590	2.130	20.12

## 2. Scrubbing the D2EHPA organic (Fig 1)

5 The aim of scrubbing is to scrub any cobalt and nickel that is inevitably co-extracted with zinc, calcium, copper and manganese, from the D2EHPA organic extraction solution to the aqueous scrub raffinate and to minimise the scrubbing of manganese, copper, calcium and zinc.

10

Two scrubbing stages were used with a combined solution of manganese (6.78 g/L) and copper (0.35 g/L) at an A/O flowrate ratio of 1:5. Scrubbing results are listed in Table 2. The cobalt and nickel scrubbing efficiencies 15 were 100% with no cobalt and nickel being left in the organic solution. This scrub raffinate containing 0.142 g/L cobalt would be recycled back to the D2EHPA extraction feed. By doing this, the cobalt and nickel recovery would approach 100%.

20

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Table 2 Summary of scrubbing test results using a combined Mn and Cu scrub solution

Metal name	Concentration (g/L)				Total scrub efficiency (%)
	Scrub solution	loaded organic	scrubbed organic	scrub raffinate	
Zn	0.000	0.255	0.256	0.000	0.00
Ca	0.035	0.605	0.610	0.054	-0.82
Mn	6.781	1.775	3.095	0.926	-41.65
Cu	0.349	0.089	0.146	0.112	-35.45
Co	0.000	0.031	0.000	0.142	100.00
Ni	0.000	0.000	0.000	0.001	100.00
Mg	0.019	0.590	0.000	2.372	100.00

5

3. Selective stripping of D2EHPA organic (Fig 1)

The aim of selective stripping is to generate a solution containing mainly manganese and copper for using as scrubbing solution in the previous stage.

10

One selective strip stage was used at an A/O flowrate ratio of 1:5 with 14.9 g/L sulphuric acid. The results are shown in Table 3. The strip raffinate contained 7.3 g/L manganese and 0.54 g/L copper, which was just slightly higher than the scrubbing solution used in the previous stage (6.78 g/L manganese and 0.35 g/L copper). However this could be easily corrected by using slightly more dilute sulphuric acid for stripping, say 12 g/L.

15 20 4. Bulk stripping of D2EHPA organic (Fig 1)

The aim of bulk stripping is to re-generate the organic D2EHPA solution by stripping all elements from the organic extractant.

25

Two bulk strip stages were used at an A/O

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flowrate ratio of 1:5 with 37 g/L hydrochloric acid. The results are also shown in Table 3. All the zinc, calcium, copper and manganese were stripped. If no calcium is present in the feed, sulphuric acid can be used for bulk 5 stripping.

Table 3 Summary of semi-continuous stripping test results  
10 with an A/O ratio of 1:5

Metal name	Concentration (g/L)			Total strip efficiency (%)
	Scrubbed organic	Stripped organic 1	Strip raffinate 1	
(Selective strip, 14.9 g/L H <sub>2</sub> SO <sub>4</sub> )				
Zn	0.256	0.255	0.022	1.73
Ca	0.610	0405	0.280	33.28
Mn	3.095	1.570	7.319	46.78
Cu	0.146	0.030	0.540	78.26
(Bulk strip, 36.6 g/L HCl)				
	Stripped organic 1	Stripped organic 2	Strip raffinate 2	
Zn	0.255	0.000	1.494	100.00
Ca	0.405	0.000	2.401	100.00
Mn	1.570	0.000	8.679	100.00
Cu	0.030	0.000	0.159	100.00

It will be understood to persons skilled in the art of the invention that various modifications could be 15 made to the preferred embodiments illustrated and described above without departing from the spirit and scope of the invention.

## CLAIMS:

1. A method of separating nickel, cobalt or both from other cations contained in a leach solution, the 5 method including the steps of subjecting the leach solution to separate solvent extraction steps using an organophosphoric acid, a carboxylic acid and an organophosphinic acid.
- 10 2. The method as claimed in claim 1, wherein the carboxylic acid extraction step is conducted with a mixture of carboxylic acid and a synergist that is capable of increasing the pH gap,  $\Delta\text{pH}_{50}$ , between isotherms for nickel and cobalt and those for manganese and calcium, wherein the 15 pH<sub>50</sub> value is the pH at which 50% metal extraction is achieved.
3. The method as claimed in claim 2, wherein the synergist is selected from the group consisting of pyridine 20 carboxylate esters, phosphine oxides and oximes.
4. The method as claimed in any one of the preceding claims, wherein the carboxylic acids is the formula RCOOH, in which R represents any optionally substituted aliphatic 25 or aromatic group, or a combination of these groups.
5. The method as claimed in claim 4, wherein R contains at least 4 carbon atoms.
- 30 6. The method as claimed in claim 4, wherein R contains between 4 and 18 carbon atoms.
7. The method as claimed in any one of the preceding claims, wherein the carboxylic acid is 2-hexyl, 2-methyl 35 octacarboxylic acid or a carboxylic acid having extraction characteristics similar to or the same as 2-hexyl, 2-methyl octacarboxylic acid.

8. The method as claimed in any one of the preceding claims, wherein the organophosphoric acid is of the formula  $(RO)_2PO_2H$ , in which each R group, which may be the same or 5 different, is an optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl group.

9. The method as claimed in claim 8, wherein each R group has a minimum of 4 carbon atoms.  
10

10. The method as claimed in claim 8, wherein each R group has between 6 to 18 carbon atoms.

11. The method as claimed in claim 8, wherein R is n- 15 octyl, cyclooctyl or 2-ethylhexyl.

12. The method as claimed in any one of claims 1 to 7, wherein the organophosphoric acid is di-2-ethylhexyl phosphoric acid, or an organophosphoric acid having 20 extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid.

13. The method as claimed in any one of the preceding claims, wherein the organophosphinic acid is of the formula 25  $R_2PO_2H$ , in which the two R groups, which may be the same or different, are selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

30 14. The method as claimed in claim 13, wherein the two R groups each contain a minimum of 4 carbon atoms.

15. The method as claimed in claim 13, wherein the two R groups each contain from 6 to 18 carbon atoms.  
35

16. The method as claimed in any one of claims 1 to 12, wherein the organophosphinic acid is di-2,4,4-

trimethylpentyl phosphinic acid or an organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentyl phosphinic acid.

5 17. The method as claimed in any one of the preceding claims, wherein a modifier is used in the organophosphoric and organophosphinic acid solvent extraction stages to facilitate phase separation of the aqueous and organic phases.

10

18. The method as claimed in claim 17, wherein the modifier is tri *n*-butyl phosphate.

15 19. The method as claimed in any one of the preceding claims, wherein the organic solvent used in the carboxylic acid, organophosphoric acid and organophosphinic acid solvent extraction stages is kerosene.

20 20. The method as claimed in any one of the preceding claims, wherein the loaded organic phase resulting from solvent extraction with organophosphoric acid is scrubbed with an aqueous scrub solution containing manganese and copper, which aqueous scrub solution is obtained by conducting a selective strip on a scrubbed loaded organic 25 solution produced in the scrubbing step, and recycling the manganese and copper-containing aqueous solution back to the scrubbing stage to be used as the aqueous scrub solution.

30 21. The method as claimed in claim 20, wherein a spent aqueous scrub solution generated in the scrubbing step is then recycled to the leach solution of the organophosphoric acid extraction step to maximise the recovery of cobalt (and nickel, if present), and the 35 selectively stripped organic is subjected to bulk stripping to remove a large proportion of the cations remaining therein to be recycled for use as the organic phase for the

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organophosphoric solvent extraction..

22. The method as claimed in claim 20 or claim 21, wherein the mole ratio of  $(\text{Mn}+\text{Cu})/(\text{Co}+\text{Ni})$  in the aqueous 5 scrub solution is at least 1.5.

23. The method as claimed in any one of the preceding claims, wherein the method does not include a sulphide precipitation stage for separating cobalt from manganese.

10 24. A method for separating nickel, cobalt or both from other cations contained in a leach solution, the method involving subjecting the leach solution to separate solvent extraction steps using:

15 (a) an organophosphinic acid; and  
(b) a carboxylic acid in combination with a synergist that is capable of increasing the pH gap,  $\Delta\text{pH}_{50}$ , between isotherms for nickel and cobalt and those for manganese and calcium.

20 25. A plant for conducting the method as claimed in any one of claims 1 to 23, the plant including, in any order:

25 - a carboxylic acid solvent extraction circuit including a carboxylic acid solvent extractor and a carboxylic acid stripper;  
- an organophosphoric acid solvent extraction circuit including an organophosphoric acid solvent extractor and an organophosphoric acid stripper; and  
30 - an organophosphinic acid solvent extraction circuit including an organophosphinic acid solvent extractor and an organophosphinic acid stripper.

26. The plant as claimed in claim 25, wherein the 35 organophosphoric acid extraction circuit includes:  
- a scrubber for scrubbing the loaded organic solution generated in solvent extractor;

- 29 -

- a selective stripper in which the scrubbed organic solution generated in the scrubber is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubber;
- 5 - a scrubbed organic solution conduit for conducting the scrubbed organic solution to the selective stripper;
- an aqueous scrub solution conduit for conducting the aqueous scrub solution from the selective stripper to the scrubber; and
- 10 - a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubber to the organophosphoric acid solvent extractor.

27. The plant as claimed in claim 26, wherein the  
15 plant further includes an organic solution recycle conduit for conducting the partially stripped scrubbed solution from the stripper to the organophosphoric acid solvent extractor.

20 28. The plant as claimed in claim 27, wherein a bulk stripper is located in the recycle conduit, in which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extractor.

25

29. The plant as claimed in any one of claims 25 to 28, the plant including cobalt and nickel recovery stages for recovering cobalt and nickel.

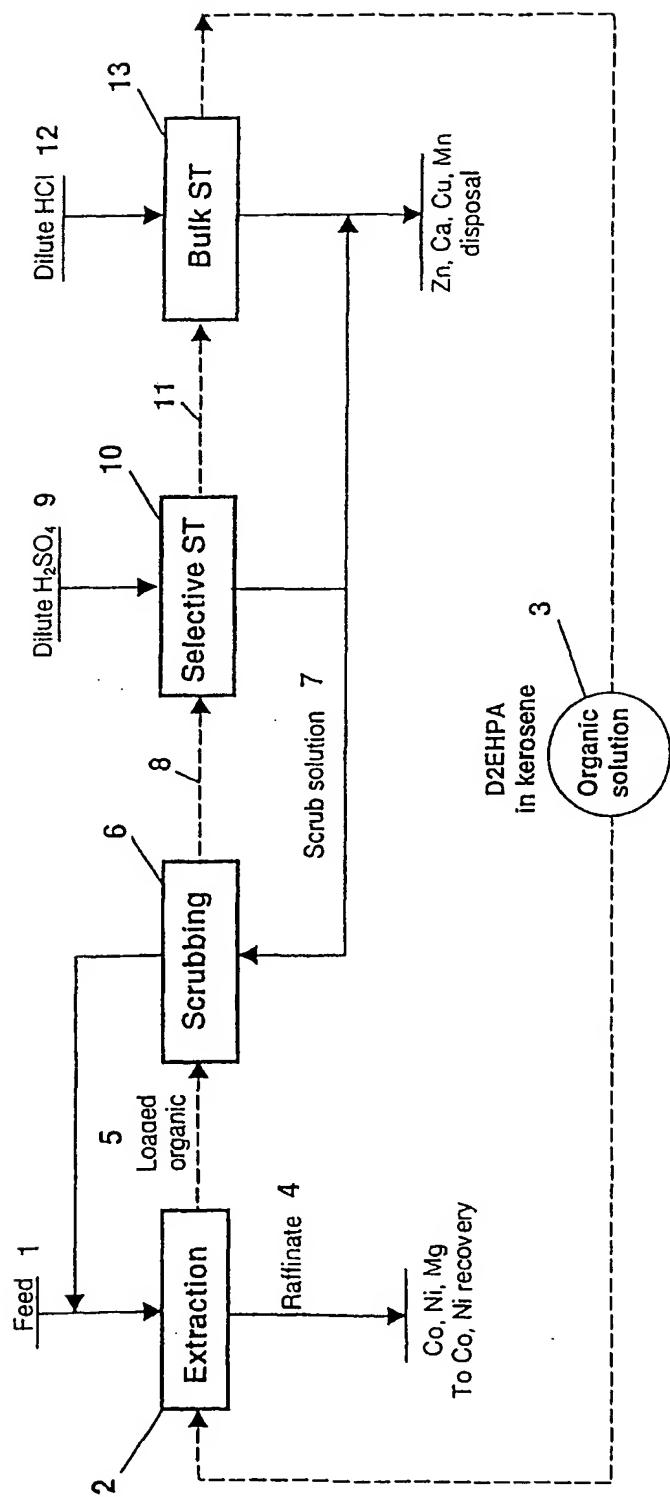


FIGURE 1

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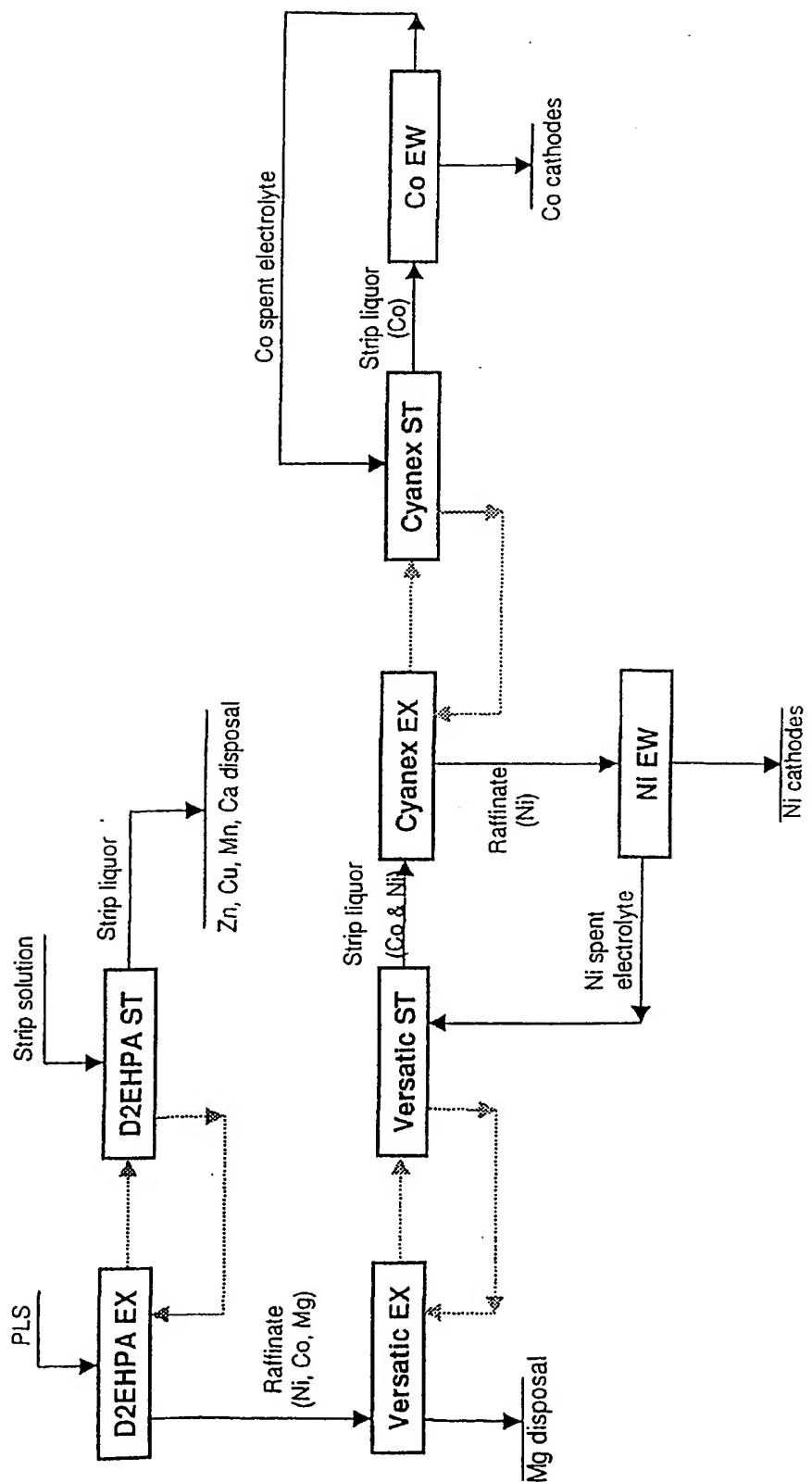


Fig 2

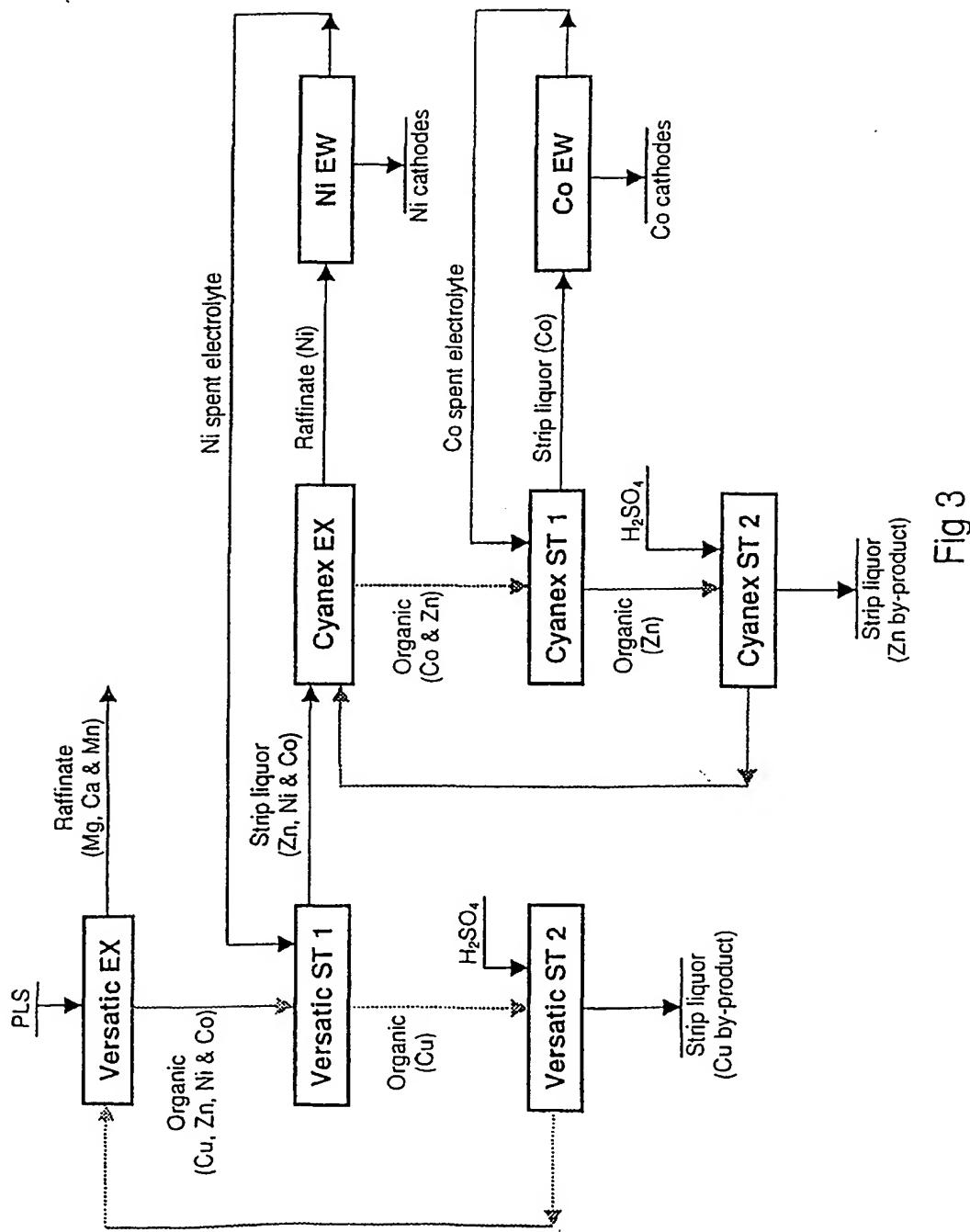


Fig 3

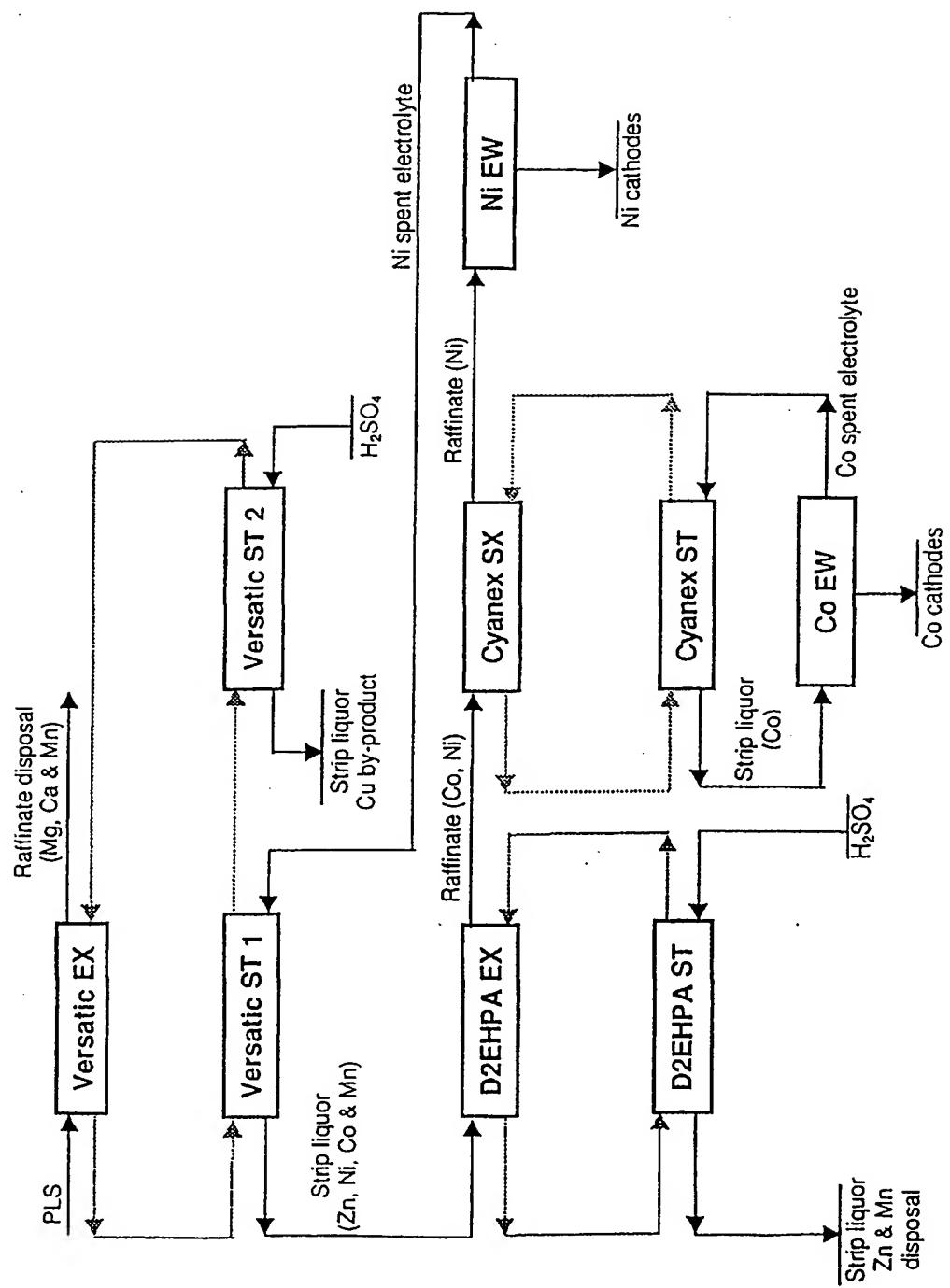


Fig 4

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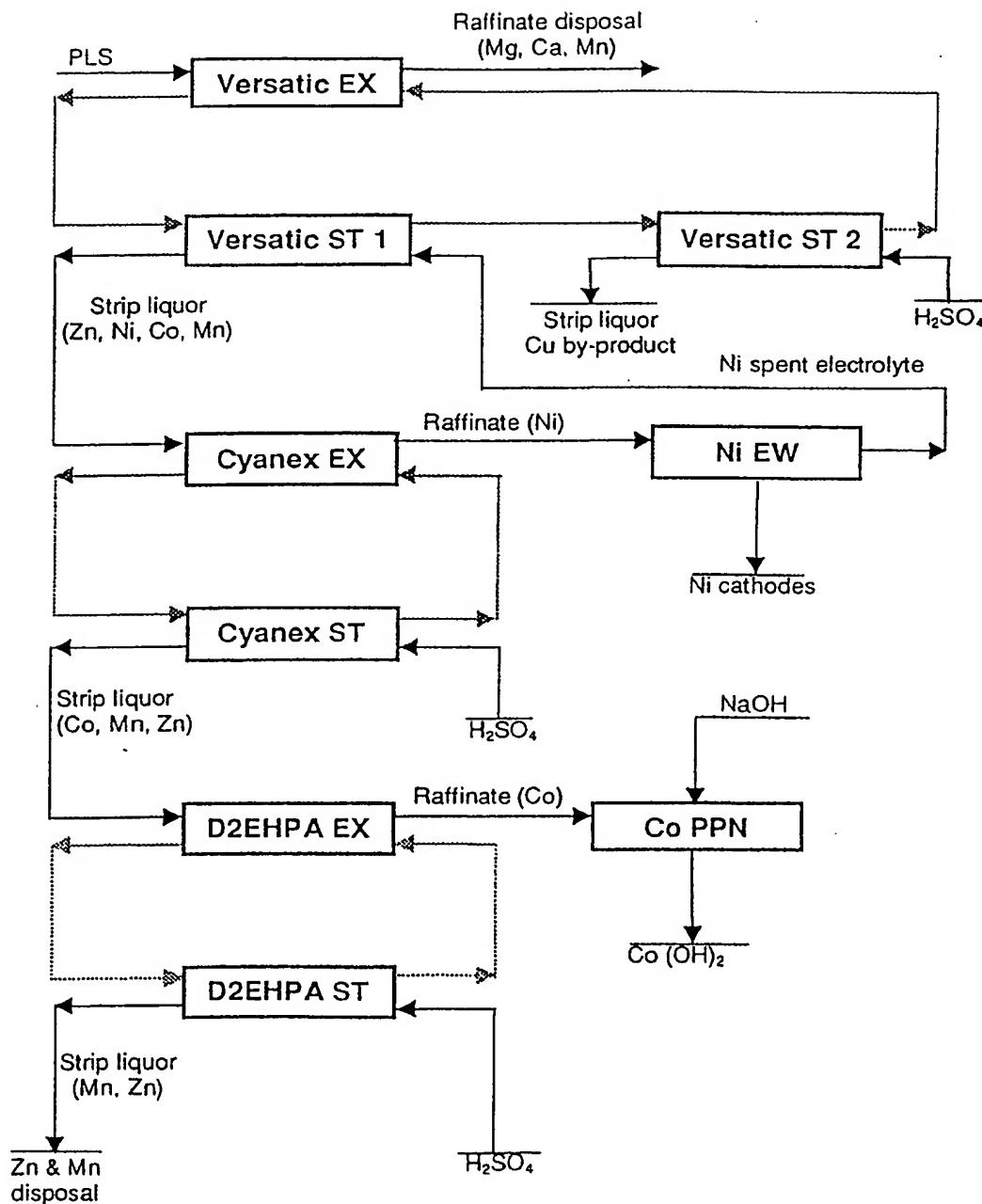


Fig 5

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU01/01161

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl. <sup>7</sup> : C22B3/26,3/32,3/38,23/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) C22B3/26,3/32,3/38,23/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU IPC AS ABOVE.		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT; nickel,cobalt,solvent,extract		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU A 40890/96 (Resolute Resources Ltd.) (18/07/96)	
A	EP A 0617135 (Preston, J.S.) (28/09/94)	
<input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search <u>17 October 2001</u>	Date of mailing of the international search report <u>30 OCT 2001</u>	
Name and mailing address of the ISA/AU  AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer  <b>G.Carter</b> Telephone No : (02) 6283	

**EINTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/AU01/01161

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
EP	061135	NONE
AU	40890/96	NONE

END OF ANNEX